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Investigating inherent differences in isotopic composition between human bone and enamel bioapatite: implications for reconstructing residential histories

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ABSTRACT

In archaeological research, human bone and enamel bioapatite isotopic compositions are commonly used to reconstruct residential and dietary histories. In doing so, enamel and bone bioapatite are implicitly treated as isotopically equivalent, but recent research has determined that carbonate–carbon and –oxygen isotopic compositions of these two tissues may be offset by several per mil. Here, we compare the isotopic compositions of co-forming bone and enamel from juvenile humans. We also assess the impact of a standard pre-treatment procedure for the removal of organic matter and exogenous carbonates on carbon- and oxygen-isotope compositions and on bioapatite crystallinity and carbonate content. Pre-treatment procedures had minimal effect on both enamel and bone carbon and oxygen isotopic compositions (±0.4–±0.9‰) and bioapatite crystallinity, and effectively removed exogenous carbonates. The offset between enamel and bone phosphate–oxygen isotopic compositions is relatively small (±0.7 ± 0.5‰). The offsets for carbonate–oxygen (+1.4 ± 1.0‰) and –carbon (+4.3 ± 1.2‰) are larger, and enamel is consistently ^{18}O- and ^{13}C-enriched relative to bone. Interpreted conservatively, phosphate–oxygen isotopic data from paired enamel and bone remain suitable for determining residential history, whereas the isotopic compositions of carbonate–oxygen and –carbon from enamel and bone bioapatite are inherently different and cannot be compared uncritically.

1. Introduction

Carbonate–carbon and –oxygen and phosphate–oxygen isotopic analyses of bioapatite from bone and tooth enamel are widely used in archaeological and palaeoenvironmental studies to investigate seasonality, mobility, and climate change, and to reconstruct palaeodiet and the ecology of past ecosystems. In archaeological research, human bone and enamel samples are commonly used to investigate changes in drinking water source ($\delta^{18}O_p$ and $\delta^{18}O_{sc}$) and to infer changes in place of residence based on natural variability in environmental water isotopic composition (*inter alia* Buzon et al., 2012; Chenery et al., 2010; Dupras and Schwarcz, 2001; Fricke et al., 1995; Hewitt, 2013; Knudson, 2009; Knudson et al., 2009; Mitchell and Millard, 2009; Perry et al., 2009; Schwarcz et al., 1991; Smits et al., 2010; Webb, 2010; Webb et al., 2013; White et al., 1998, 2000, 2002, 2004a, 2004b, 2007). This research is based on the well-established relationship between the oxygen-isotope compositions of mammalian body tissues and consumed water, including drinking water and, to a lesser extent, food water and respired oxygen (Bryant and Froelich, 1995; Luz and Kolodny, 1985; Stuart-Williams and Schwarcz, 1997). Drinking water oxygen-isotope values ($\delta^{18}O_{dw}$) reflect the isotopic composition of environmental water, including both meteoric and recycled water (Luz and Kolodny, 1985; Stuart-Williams and Schwarcz, 1997), and this isotopic ratio is incorporated into body tissues (adjusted by a metabolic fractionation factor). Carbon-isotope data ($\delta^{13}C_{sc}$) are further used to reconstruct diet and dietary change between childhood and adulthood, and, with carbon- and nitrogen-isotope compositions of protein, can be used to create a more informative dietary reconstruction. The $\delta^{13}C_{sc}$ values of bioapatite reflect the total macronutrient content of diet, in contrast to $\delta^{13}C$ values of collagen, which reflect the isotopic composition of dietary protein. Natural isotopic variability in carbon-isotope compositions begins at the base of the food web, where different plants discriminate

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against ^{13}C to differing degrees based on photosynthetic pathway (i.e., C_3 versus C_4 plants). This variability is transmitted through the food web and is ultimately reflected in the $\delta^{13}C_{sc}$ values of consumers (Ambrose and Norr, 1993; DeNiro and Epstein, 1978; Howland et al., 2003; Jim et al., 2004; Kellner and Schoeninger, 2007; Tieszen and Fagre, 1993).

Isotopic studies make valuable contributions to understanding migration and residential histories in archaeological societies and in the hominid evolutionary past. There are numerous ways in which isotopic data can inform residential mobility by, for example, assessing relative isotopic variability within a sample, comparing human isotopic data to environmental or geological baseline data, or comparing multiple or paired tissues from the same individual to create a residential history. The validity of comparing isotopic data from paired bone and enamel samples from one individual, or the comparison of bone and enamel isotopic values among different individuals, rests on the assumption that the bioapatite in enamel and bone records $\delta^{13}C_{sc}$, $\delta^{18}O_{sc}$ and $\delta^{18}O_p$ values in a similar fashion and that there are no differences in fractionation between the two tissues. Recent research involving pigs has demonstrated that there are large, consistent offsets in carbonate–oxygen and –carbon between enamel and bone forming at the same time (+2.3‰ for $\delta^{13}C_{sc}$, +1.7‰ for $\delta^{18}O_{sc}$; Warinner and Tuross, 2009). An offset of similar magnitude was not, however, found in a controlled growth and feeding study of rats (Luz and Kolodny, 1985) for phosphate-oxygen isotopic compositions. Instead, a minor and inconsistent offset of ±0.5 ± 0.6‰ was determined. Here, our objectives are to assess the inherent offset between enamel and bone bioapatite isotopic compositions for both phosphate-oxygen and carbonate-carbon and -oxygen in humans. More specifically, we will compare paired bone and enamel isotopic data from children less than 12 years of age in order to estimate the expected offset between tissues growing at approximately the same time under 'normal' conditions of growth and food and water consumption. We use Fourier Transform Infrared spectroscopy (FTIR) to monitor changes in bioapatite structure related to diagenesis, and to detect any anomalous materials (e.g., calcite) in the samples. We will also assess the impact of a common pre-treatment protocol for the removal of organic material and secondary carbonates on carbonate isotopic data and FTIR parameters.

2. Background

2.1. Research design

The individuals selected for this study were juveniles less than 12 years of age, chosen with the objective of minimising inter-tissue differences caused by bone and enamel mineralisation occurring during different periods of an individual's lifetime. Tissues forming at different times during an individual's life could induce isotopic differences that result from changing patterns of water and food consumption as adults relative to childhood, rather than inherent biological differences. For children aged 4–6 years, 1st molars and associated bone were sampled. Any influence on oxygen-isotope compositions resulting from breastfeeding is expected to be represented in both bone and 1st molar enamel for the younger children, so no adjustment was made to compensate for ^{18}O-enrichment of tissues formed before weaning (as in White et al., 2000, 2004b). For slightly older children (aged 4–12 years), 2nd molars and associated bone were sampled. All teeth selected had well-mineralised crowns and partially or fully formed roots. Bone turnover occurs at a rate of 10–30% per year for adolescents (Hedges et al., 2007) and as high as 100% per year for very young children (Nanci et al., 2003); thus, although the period of time represented by bones and teeth does overlap, the tissues may not be entirely co-forming. An additional important consideration is that all of the children died at a young age from unknown disease processes or stressors, which could have impacted their metabolism in unknowable ways.

2.2. FTIR parameters

FTIR spectroscopy is routinely used to assess post-mortem recrystallization, deposition of secondary carbonates, and the ratio of carbonate to phosphate present in bone and enamel samples. Although this methodology does not directly assess biochemical preservation, FTIR does describe the bioapatite structure and detects aberrant materials, such as calcite, adsorbed from the burial environment. Commonly used parameters included in this study are crystallinity indices (CI) and carbonate-phosphate ratios (CO_3/PO_4), as well as B-carbonate on phosphate indices (BPI), used to assess substitution of carbonate for type B trivalent phosphate ions, and weight percent carbonate content (LeGeros, 1991; Pucéat et al., 2004; Sponheimer and Lee-Thorp, 1999; Shemesh, 1990; Surovell and Stiner, 2001; Weiner and Bar-Yosef, 1990; Wright and Schwarcz, 1996).

Crystallinity indices were determined using the following formula: $[605_{ht} + 565_{ht}] / 590_{ht}$, where 'ht' represents the height of the bands or valleys at the positions specified. Crystallinity indices for fresh bones are approximately 2.8–3.0, and typically range from 3.5–4.8 for archaeological samples. A crystallinity index that is higher than 4.3 suggests extensive recrystallization, and therefore poor bioapatite preservation (Stuart-Williams et al., 1998; Wright and Schwarcz, 1996). Carbonate/phosphate (CO_3/PO_4) ratios are calculated as follows: $1415_{ht}/1035_{ht}$; typically, modern bones have CO_3/PO_4 ratios of ~0.5 and unaltered enamel has a slightly lower ratio (Smith et al., 2007; Wright and Schwarcz, 1996). Archaeological material that has lower CO_3/PO_4 ratios is assumed to have lost carbonate to the burial environment, whereas higher CO_3/PO_4 ratios suggest addition of secondary carbonate from the burial environment (Smith et al., 2007). BPI is calculated as: $1415_{ht}/605_{ht}$ and describes B-site carbonate content. Using the BPI, weight % carbonate can be estimated using the following equation: 10 * BPI+0.7 (LeGeros, 1991), and this estimate provides a more intuitive description of the presence of carbonate in the sample. Using this formula, unaltered bone should contain ~7.4 wt.% carbonate and enamel ~3.5 wt.% carbonate (LeGeros, 1991). Spectra were also visually inspected for aberrant peaks, particularly near 710 cm^{-1}, which indicate the presence of calcite, and a shoulder at 1096 cm^{-1}, which indicates that francolite may have formed. Based on Garvie-Lok et al. (2004), CI and CO_3/PO_4 ratios should not change significantly with pre-treatment. The BPI and wt. $\%CO_3$ estimates will likely decrease for some samples due to the removal of secondary/adsorbed carbonate.

2.3. Impact of pre-treatment procedure on carbonate–oxygen and –carbon isotopic compositions

Bone and enamel destined for carbonate-carbon and –oxygen isotopic analysis are typically subjected to some form of pre-treatment protocol, the objective of which is to remove organic matter, as well as adsorbed carbonate and exogenous carbonate-containing material. It is believed that adsorbed carbonate, which adheres to the surface of bioapatite mineral[1] is likely to be contaminated both by exogenous carbonates (e.g., calcite) from the burial environment and through isotopic exchange and bioapatite

[1] As opposed to structural carbonate, which substitutes *in vivo* in either the OH^- or PO_4^{3-} positions of bioapatite ($Ca_{10}(PO_4)_6(OH)_2$).

Table 1
Sample summary.

Sample ID[a]	Age in years[b]	Tooth type	Bone type sampled
MG12/5	4–6	LLM1	Left mandibular body
MG14/8	4	LRM1	Right mandibular body
MG14/28a	5.5–6.5	URM2	Right temporal
MG204b	5	LRM1	Right mandibular body
SP2	4–5	LRM2	Right mandibular body
SP10k	8	LRM2	Left mandibular body
SP11-2/2	9–10	LLM2	Left mandibular body
SP11-2/7b	9–12	LRM2	Right zygoma
SP17-6/2	4.5–6	URM2	Right mandibular ramus
SP17-6/3	9–10	LRM2	Right mandibular body

[a] MG: Marco Gonzales, SP: San Pedro.
[b] Based on dental ageing.

recrystallization (Lee-Thorp, 1989). Adsorbed carbonate is also relatively more soluble than structural carbonate, and pre-treatment protocols exploit this difference in solubility. Isotopic shifts associated with various pre-treatment protocols using modern material (thus eliminating the potential influence of diagenetic material) are summarised in Garvie-Lok et al. (2004) and Koch et al. (1997). From their data, we expect the following changes in isotopic composition resulting from the removal of adsorbed carbonate via pre-treatment: −0.5 to −1.0‰ for $\delta^{13}C_{sc}$ and +2.0 to +3.0‰ for $\delta^{18}O_{sc}$ for bone, and −0.5 to −1.0‰ for $\delta^{13}C_{sc}$ and +1.0‰ for $\delta^{18}O_{sc}$ for enamel. Assuming that post-mortem alteration has not severely impacted the bioapatite structure and, by inference, biogenic isotopic compositions, there should be no strong correlation between isotopic data and any FTIR parameter. We expect that change in sample weight through pre-treatment to remove organic matter and adsorbed carbonates (expressed as % yield) may correlate with BPI and estimated wt. % carbonate content, which describe carbonate presence in bioapatite.

2.4. Expectations for phosphate–oxygen and carbonate–carbon and –oxygen isotopic data

The primary focus of this study is to determine if there is a consistent ^{13}C- or ^{18}O-enrichment of enamel over bone (or vice versa) that is larger than the analytical error associated with our methodologies. Based on controlled growth and feeding experiments using rats (Luz and Kolodny, 1985), we expect that inter-tissue offsets for phosphate-oxygen isotope values will be ≥±0.5‰ and ≤±1.0‰ for $\delta^{18}O_p$; differences of less than ±0.2‰ fall within analytical error (see 3.3). We expect that inter-tissue offsets between enamel and bone $\delta^{18}O_{sc}$ and $\delta^{13}C_{sc}$ values will be larger, similar to offsets observed by Warinner and Tuross (2009) in pigs (+2.3‰ for $\delta^{13}C_{sc}$, +1.7‰ for $\delta^{18}O_{sc}$).

3. Sampling and methods

3.1. Sample description

Enamel and bone samples were collected from ten juveniles[2] with well-preserved dentition and bone in association with teeth. For younger children (mean age 5 years), 1st molars were taken, and for older children (mean age 7.5 years), 2nd molars (Table 1). Age was assessed using dental eruption (Scheuer and Black, 2004) and bone samples were taken either from the mandible from which the tooth was extracted, or from attached craniofacial bone. All samples are from individuals excavated at the ancient Maya sites of Marco Gonzales and San Pedro located on Ambergris Caye, Belize from 1986 to 1993 and curated in the Department of Anthropology at The University of Western Ontario, London, Canada. Samples from Marco Gonzales have been dated to the late Preclassic to late Postclassic (100 B.C.E. to AD1350), and San Pedro samples have been dated to the Terminal Postclassic to Historic period (AD1400–1650). A more comprehensive sample set from these two sites has been analysed for carbon, nitrogen and carbonate-carbon isotopic compositions (Williams et al., 2005, 2009). All samples included in this study were, however, re-analysed using the analytical methods described below. FTIR spectroscopy was used to assess bioapatite preservation; parameters included here are crystallinity indices, carbonate-phosphate ratios, B-carbonate on phosphate indices and estimated weight percent carbonate content. The FTIR spectra were also examined for secondary calcite, fluoridation, and other anomalies. Stable isotope analyses for phosphate-oxygen and carbonate-carbon and -oxygen were performed on all bone and enamel samples, and at least 10% duplicate samples were also analysed. To assess pre-treatment effects, all samples were analysed as untreated and pre-treated replicates for both FTIR and carbonate-carbon and -oxygen isotopic analyses. All analyses were performed in the Laboratory for Stable Isotope Science at The University of Western Ontario, London, Canada.

3.2. FTIR methodology

Approximately 2 mg of finely powdered bone or enamel (grain size 45–65 μm) was mixed with 200 mg potassium bromide and compressed with a hydraulic press at 10 tons for 10 min to create a pellet. Absorbance spectra were obtained using a Bruker Vector 22 FTIR Spectrometer, scanning 16 times from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Samples of bone and enamel were analysed twice as untreated and pre-treated replicates (see 3.4).

3.3. Phosphate–oxygen isotopic analysis

For each bone or enamel sample, 30–35 mg of powder was dissolved in 3 M acetic acid, and silver orthophosphate (Ag_3PO_4) was precipitated using the ammonia volatilization method (Firsching, 1961; Stuart-Williams and Schwarcz, 1995). Carbon dioxide was produced offline by reacting Ag_3PO_4 with bromine pentafluoride at 600 °C for at least 16 h, and then converting O_2 to CO_2 over red-hot graphite (adapted from Clayton and Mayeda, 1963; Crowson et al., 1991). Oxygen-isotope ratios of CO_2 were measured using a Thermo Scientific Delta V Plus isotope ratio mass spectrometer operating in dual inlet mode. Consistency of oxygen extraction was monitored using an Aldrich silver phosphate standard. The efficacy of the Ag_3PO_4 precipitation was tested by examining the relationship between the amount of Ag_3PO_4 precipitated and the $\delta^{18}O_p$ values. There was no significant correlation found for either bone (Spearman's $\rho = 0.532$, $p = 0.141$) or enamel (Spearman's $\rho = 0.393$, $p = 0.295$), indicating that one isotope (^{16}O vs. ^{18}O) was not preferentially precipitated. Methodological reproducibility and analytical precision, determined through duplicate sample precipitation, extraction and analysis, was ±0.2‰. The average observed $\delta^{18}O$ value for Aldrich Ag_3PO_4 was +11.1 ± 0.3‰ (1σ), which compares well with the expected value of +11.2‰.

3.4. Carbonate–carbon and –oxygen isotopic analysis

Bone and tooth samples were mechanically cleaned and ground to ≤180 μm. Between 10 and 14 mg of bone or enamel powder was treated with 2% sodium hypochlorite (NaOCl) for 24 (enamel) or 72 (bone) hours to remove organic material, rinsed with Millipore

[2] Only nine individuals were used for phosphate–oxygen isotopic analysis due to sample size constraints.

water, and then treated with 0.1 M acetic acid for four hours to remove secondary/adsorbed carbonates. Samples were rinsed with Millipore water and freeze-dried for more than 24 h before weighing to assess sample loss resulting from the pre-treatment procedure. Approximately 1.0 mg of sample was reacted with an excess of H_3PO_4 under vacuum at 90 °C for 25 min using a Micromass MultiPrep autosampling device. The CO_2 gas produced was analysed using a VG Optima dual-inlet isotope ratio mass spectrometer coupled to the MultiPrep autosampler. A series of standards was analysed with samples under the same conditions during each analytical session. The $\delta^{13}C$ values were calibrated relative to VPDB using NBS-19 and LSVEC, and the $\delta^{18}O$ values were calibrated relative to VSMOW using NBS-19 and NBS-18. Reproducibility was established through methodological and analytical duplicates, and was found to be ±0.1‰ for carbon and ±0.4‰ for oxygen. Accuracy was assessed using an internal calcite standard (WS-1), and was found to be ±0.1‰ for carbon and ±0.2‰ for oxygen (average difference from expected values). The average observed $\delta^{18}O$ value for WS-1 was +26.4 ± 0.2‰ (1σ) and +0.8 ± 0.1‰ (1σ) for carbon; these compare well with the expected values of +26.2‰ and +0.8‰ for oxygen and carbon, respectively.

4. Results

4.1. FTIR Parameters

Because all sample numbers are small (n = 10 for each tissue type), statistics are used descriptively, i.e., no statistical significance is reported. Fig. 1 shows typical spectra obtained for bone and enamel before and after pre-treatment. Before pre-treatment, average bone CI was 3.1 ± 0.3 and for enamel, 3.2 ± 0.3. These values suggest that both tissues are well-preserved. The average CO_3/PO_4 ratios were 0.5 ± 0.2 for bone and 0.2 ± 0.0 for enamel, indicating minimal addition/loss of carbonate for bone. The average BPI for bone was 1.1 ± 0.4 and 0.5 ± 0.1 for enamel. Using these BPI values, the average estimated weight %CO_3 was 11.6 ± 4.0% for bone and 5.9 ± 0.9% for enamel. When B-12/5, which contains secondary calcite from the burial environment (710 cm^{-1} peak present; Fig. 2), is excluded from the bone average, the BPI decreases to 1.0 ± 0.2 and weight %CO_3 to 10.5 ± 2.0%. These weight %CO_3 values are slightly higher than expected (7.4% and 3.5% for bone and enamel, respectively), suggesting some addition of exogenous carbonate from the burial environment. All parameters are reported as average ±1σ, and are summarized in Table 2 and Fig. 3 (see also Table S1).

After pre-treatment, the average bone CI was 3.0 ± 0.3 and for enamel, 3.1 ± 0.2. The average CO_3/PO_4 ratios were 0.3 ± 0.1 for bone and enamel. The change in ratios for bone indicates that adsorbed exogenous carbonates were likely removed, and, for B-12/5, the secondary calcite peak can no longer be observed (Fig. 2). The average BPI was 0.7 ± 0.1 for pre-treated bone and 0.6 ± 0.1 for enamel. Weight % CO_3 content was estimated to be 8.0 ± 1.2% for bone and 6.7 ± 1.3% for enamel. With the exception of the calcite-containing sample B-12/5, most of the changes in FTIR parameters were, as expected, minimal.

4.2. Phosphate–oxygen isotopic results

The expected Ag_3PO_4 precipitate yields for this procedure for archaeological bone range from 70 to 90%, although higher yields are possible, and are indeed typical for enamel, due to the greater mass of Ag^+ relative to Ca^{2+}. The Ag_3PO_4 precipitate is itself a heterogeneous substance, where larger crystals and finer grains have different isotopic compositions, and incomplete precipitations result in low precipitate yields and high $\delta^{18}O_p$ values (Stuart-

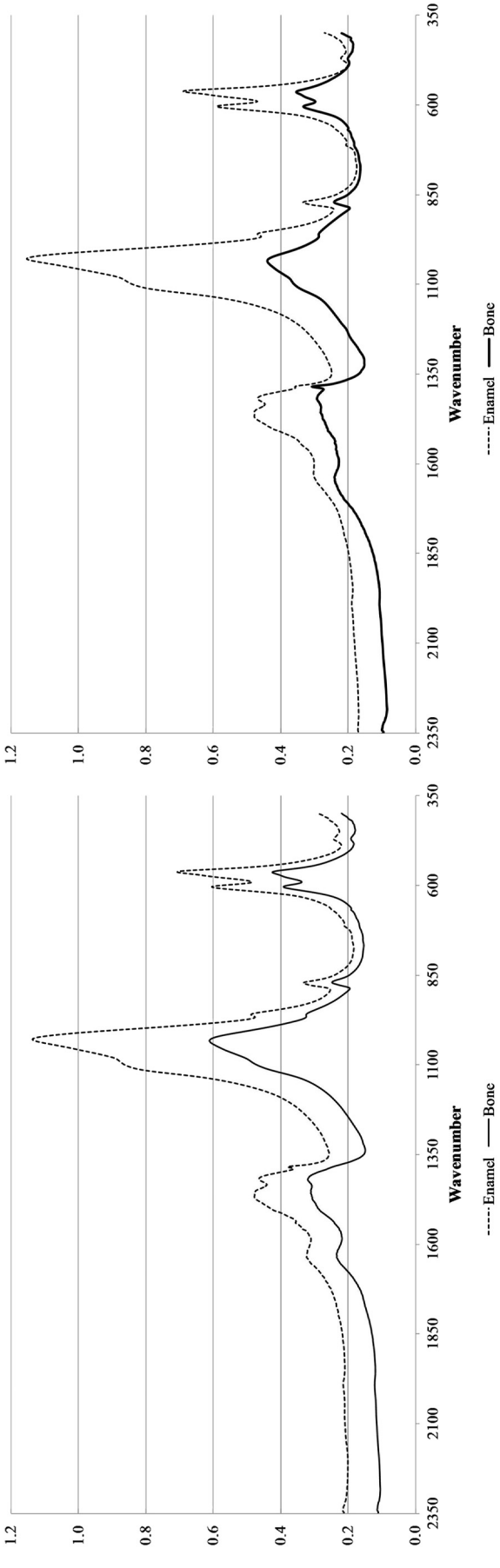

Fig. 1. Untreated (left) vs. Pre-treated (right) Bone and Enamel FTIR Spectra (B-2 and E-2).

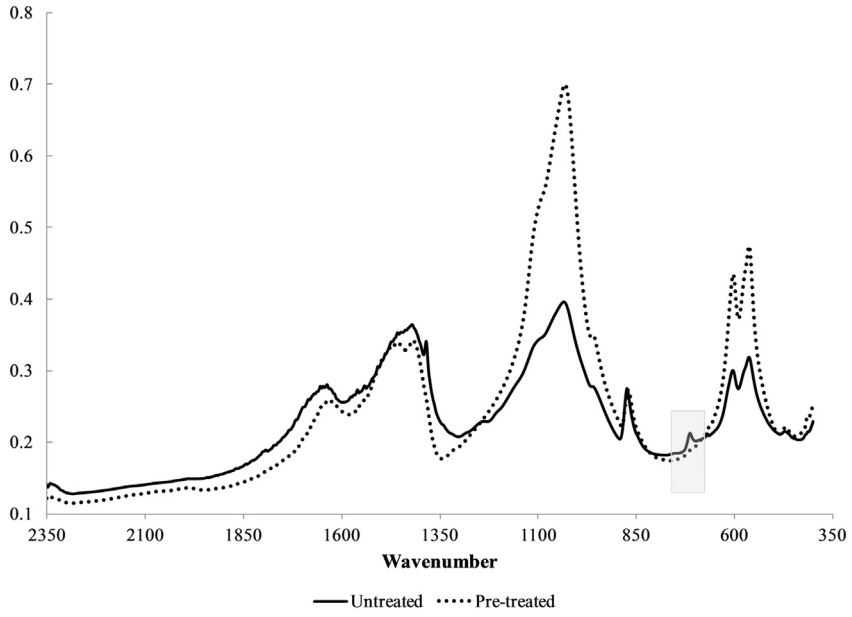

Fig. 2. FTIR Spectra for B-12/5 (grey box: secondary calcite).

Williams, 1996). Organic material was removed by heating at 95 °C in 6 M HNO_3 and 30% H_2O_2 solution. Residual organic material can strongly impact $\delta^{18}O_p$ values, and causes low yields and discoloured precipitate. Phosphate-oxygen isotopic results are shown in Fig. 4 and presented in Table 3. All values are reported as average±1σ. The average bone yield was 100 ± 10%, and ranged from 71 to 115%. The average enamel yield was 110 ± 20%, ranging from 80% to 135%. All precipitate yields fall within or exceed the expected yields, indicating that precipitations were successful and that accurate $\delta^{18}O_p$ values could be obtained. All samples produced precipitates that were yellow-gold to yellow-green in colour and were dominated by large, flake-like crystals. Finally, the theoretical CO_2 yield for this procedure is 4.8 μmol/mg of sample reacted. For this study, the average bone yield was 5.0 ± 0.2 μmol/mg and enamel yield was 5.1 ± 0.3 μmol/mg, which compare well with the theoretical yield.

The average bone $\delta^{18}O_p$ value was +17.3 ± 1.1‰, and +17.1 ± 1.1‰ for enamel. There were no strong relationships observed between either enamel or bone $\delta^{18}O_p$ values and CO_2 yields, CI or CO_3/PO_4 ratios. The absence of such relationships indicates that variability was not introduced into the dataset by any part of the methodology employed, and that post-mortem alteration is unlikely to have had an important impact on the retention of biogenic isotopic compositions. Moreover, there does not appear to be a strong correlation between age and enamel-bone differences (Pearson's R = 0.13). Individual enamel-bone differences[3] range from −1.4 to +0.9‰, with a median of −0.1‰, and the absolute average inter-tissue offset was ±0.7 ± 0.5‰.[4]

4.3. Carbonate–carbon and –oxygen isotopic results

4.3.1. Effects of pre-treatment on bone and enamel

Although the differences in FTIR parameters for untreated and pre-treated bone and enamel samples are minimal, pre-treatment did result in sample loss, reported as % yield in Table 4. The average sample yield after pre-treatment for bone is 86 ± 6% (range 77–93%). Sample loss is expected for bone, since pre-treatment involves removal of organic material (~22% by weight in fresh bone, but less in archaeological bone; Hedges and Law, 1989; Collins et al., 2002). Similarly, secondary carbonate will, based on estimates using BPI and LeGeros' formula before and after pre-treatment, comprise an average of 3.6% by weight. In contrast, enamel contains less organic material (1% by weight; Nanci, 2003) and typically little to no secondary carbonate. The average % yield for enamel is 94 ± 4% (range 88–100%). There is a strong relationship between % yield after pre-treatment and wt. % carbonate for bone and enamel before pre-treatment (n = 20; Pearson's $R = -0.837$, $p < 0.01$; Fig. 5).

The change in isotopic compositions following pre-treatment is minimal for the most part. For bone, there is no consistent shift in isotopic compositions (Table 4). Differences between pre-treated and untreated bone range from −1.7 to +0.5‰ (median +0.1‰) for carbon and from −0.7 to +2.2‰ (median +0.7‰) for oxygen. The absolute average difference (pre-treated − untreated) for carbon is ±0.4 ± 0.5‰ and for oxygen is ±0.9 ± 0.7‰. For enamel, pre-treatment generally resulted in a slight increase in carbon- and oxygen-isotope compositions. Differences between pre-treated and untreated enamel range from +0.1 to +1.9‰ (median +0.7‰) for carbon and from −0.1 to +1.3‰ (median +0.7‰) for oxygen. The absolute average difference for carbon is ±0.8 ± 0.6‰ and for oxygen is ±0.6 ± 0.5‰.

4.3.2. Inter-tissue offsets for carbon and oxygen isotopic data

Carbonate–carbon and –oxygen isotopic results are presented in Table 4 and Fig. 6. All values are reported as average ±1σ. For the inter-tissue comparison, only pre-treated bone and enamel isotopic data were used, but the difference between pre-treated and untreated offsets was small (≤0.5‰). The average bone $\delta^{13}C_{sc}$ value was −5.9 ± 0.9‰ and the average bone $\delta^{18}O_{sc}$ value was +25.3 ± 1.1‰. For enamel, the average $\delta^{13}C_{sc}$ value was −1.6 ± 1.5‰ and the average $\delta^{18}O_{sc}$ value was +26.6 ± 0.9‰. There are no strong relationships between the carbon- or oxygen-isotope results and CO_3/PO_4 ratio, CI, estimated wt. %CO_3 or % yield for bone or for enamel, suggesting that post-mortem alteration does not significantly influence the isotopic results for these

[3] Calculated as $\delta^{18}O_{p\text{-enamel}} - \delta^{18}O_{p\text{-bone}}$. Enamel-bone ranges for $\delta^{13}C_{sc}$ and $\delta^{18}O_{sc}$ were determined similarly.

[4] Absolute average differences were calculated as the mean of individual unsigned $\delta^{18}O_{p\text{-enamel}} - \delta^{18}O_{p\text{-bone}}$. Absolute average differences for $\delta^{13}C_{sc}$ and $\delta^{18}O_{sc}$ were determined similarly.

Table 2
Change in FTIR parameters with pre-treatment (after − before).[a]

Sample ID[b]	ΔCI	$\Delta CO_3/PO_4$	ΔBPI	ΔEst.%CO_3
B-12/5	0.0	−0.5	−1.3	−12.9
B-14/8	0.0	−0.1	−0.2	−2.0
B-204b	−0.1	−0.1	−0.3	−2.5
B-14/28a	0.0	−0.1	−0.1	−1.3
B-2	0.0	−0.2	−0.3	−2.6
B-10k	−0.5	0.0	0.0	−0.4
B-11-2/2	0.0	−0.1	−0.2	−1.8
B-11-2/7b	−0.2	−0.2	−0.5	−4.6
B-17-6/2	−0.2	−0.1	−0.3	−3.4
B-17-6/3	−0.1	−0.2	−0.4	−4.0
Average	−0.1	−0.1	−0.4	−3.6
1σ	0.1	0.2	0.4	3.5
E-12/5	−0.4	0.1	0.0	0.4
E-14/8	0.0	0.0	0.1	1.3
E-204b	−0.2	0.2	0.5	4.5
E-14/28a	−0.2	0.0	−0.1	−1.1
E-2	0.0	0.0	−0.1	−1.0
E-10k	0.0	0.0	0.1	1.1
E-11-2/2	0.0	0.0	0.1	1.0
E-11-2/7b	0.0	0.0	0.1	1.0
E-17-6/2	−0.2	0.0	0.0	−0.2
E-17-6/3	−0.1	0.0	0.0	0.5
Average	−0.1	0.0	0.1	0.8
1σ	0.1	0.1	0.2	1.6

[a] Raw data in Supplementary Table 1.
[b] Prefixes indicating archaeological site (SP and MG) have been replaced with B: bone sample, E: enamel sample.

samples. There was also no strong relationship between age and enamel-bone offset for carbon (Pearson's $R = 0.19$) or for oxygen (Pearson's $R = -0.18$). Enamel-bone offsets are large and consistent for both the carbon and oxygen isotopic datasets. For carbon, the average offset was +4.3 ± 1.2‰ and for oxygen, +1.4 ± 1.0‰.

5. Discussion

5.1. FTIR parameters

The archaeological samples used in this study were taken from similar depositional environments and all bone and enamel samples are well-preserved (but see B-12/5 below). All CI values fall within or below the accepted range for archaeological samples, and indicators of carbonate content show minimal addition of carbonate from the burial environment. The small increase in CO_3/PO_4 ratios, BPI and % CO_3 for some enamel samples does not indicate added carbonate. There was no exposure to a carbonate source during pre-treatment, and this is supported by the inconsistency of the change (i.e., not all samples had higher CO_3/PO_4 ratios after pre-treatment). This phenomenon was also observed by Garvie-Lok et al. (2004) and Nielsen-Marsh and Hedges (2000). It is likely an artefact of a change in relative intensities of the CO_3 and PO_4 bands, i.e., the CO_3 band changes more due to pre-treatment than does the PO_4 band, rather than an indication of contamination.

The removal of the 710 cm^{-1} peak by pre-treatment for sample B-12/5 indicates that the relatively weak pre-treatment protocol used here effectively removes calcite without inducing significant changes in crystallinity, which suggests that no unwanted secondary processes (e.g., dissolution and recrystallization) have occurred. Moreover, the strong correlation identified between estimated weight % carbonate content before pre-treatment and weight % yield of sample after pre-treatment further supports the efficacy of the pre-treatment protocol in removing exogenous carbonates. Although pre-treatment to remove exogenous carbonates and organic matter may not always be necessary, it is not possible to determine the significance of any contamination or recrystallization without a visual inspection of FTIR spectra (or another similar assessment) and the calculation of both CI and CO_3/PO_4 or BPI parameters.

5.2. Inter-tissue differences in phosphate–oxygen isotopic compositions

Neither enamel nor bone had consistently higher $\delta^{18}O_p$ values; rather, the data suggest that either scenario is equally likely to occur. The variability in the data presented here is consistent both in magnitude and in nature with Luz and Kolodny's (1985) research. Under controlled conditions, they also observed either bone or enamel having the higher value, as well as a few offsets greater than 1‰. Examination of FTIR parameters and observations during laboratory analyses did not reveal anything distinctive or unusual about the two samples with slightly larger offsets (MG14/28a, −1.4‰ and SP10k, −1.2‰). Sample MG14/28a had slightly lower bone precipitate yields than other bone samples (80%), but crystals were large and of optimal colour. The CO_3/PO_4 ratios were less than 0.5 for both bone and enamel, indicating no added carbonate and minimal loss from bone. The CIs were the highest in the sample group (~3.6 for both tissues), but, again, this is not unexpected for archaeological material. No unusual peaks were observed on the FTIR spectra (Supplementary Fig. 1). Samples from SP10k had normal Ag_3PO_4 yields (>100%) and normal appearance of precipitate. The CI and CO_3/PO_4 values are within acceptable ranges. The CI decreases substantially with pre-treatment for B-10k, suggesting some change in bioapatite crystallinity, but since other parameters assessing carbonate content do not change, it is unlikely that the change in CI indicates significant removal of exogenous carbonates. No unusual peaks are observed in the FTIR spectra (Supplementary Fig. 2). Thus, these slightly larger offsets are unlikely to be the result of diagenetic alteration or methodological inconsistency.

As mentioned above, Luz and Kolodny observed offsets of up to ±1.5‰ for rats across different groups in their controlled growth and water consumption study. Although a larger human sample size might change the average enamel-bone offset, there is excellent agreement between Luz and Kolodny's data (±0.5 ± 0.6‰, $n = 20$) and the human data presented here (±0.7 ± 0.5‰, $n = 9$), and the larger offsets fall within (SP10k) or close to (MG14/28a) one standard deviation of the average value. Individual variability in metabolic fractionation and tissue turnover rates (i.e., due to health) may instead be a plausible explanation for the larger offsets observed, induced perhaps by antemortem illness or stressors that are not detectable in the skeletal remains.

The data reported here support the use of phosphate-oxygen isotopic data from paired bone and enamel samples to investigate change in drinking water source and, by inference, change in place of residence between childhood and adulthood. The inherent offset of ±0.7 ± 0.5‰ is large enough, however, that differences of less than 1.0‰ should not be interpreted as meaningfully different, and that differences >1.0‰ and <1.5‰ should be interpreted cautiously. For example, a conservative approach to distinguishing normal variation from informative variation would be to establish a ±1.5‰ cut-off based on inherent variation in enamel and bone bioapatite phosphate-oxygen, and to use local environmental water baseline isotopic data to further constrain the attribution of place of residence based on calculated drinking water oxygen-isotope compositions.

5.3. Inter-tissue differences in carbonate–carbon and –oxygen isotopic data

Changes in carbon– and oxygen-isotope compositions associated with pre-treatment are lower than expected based on previous

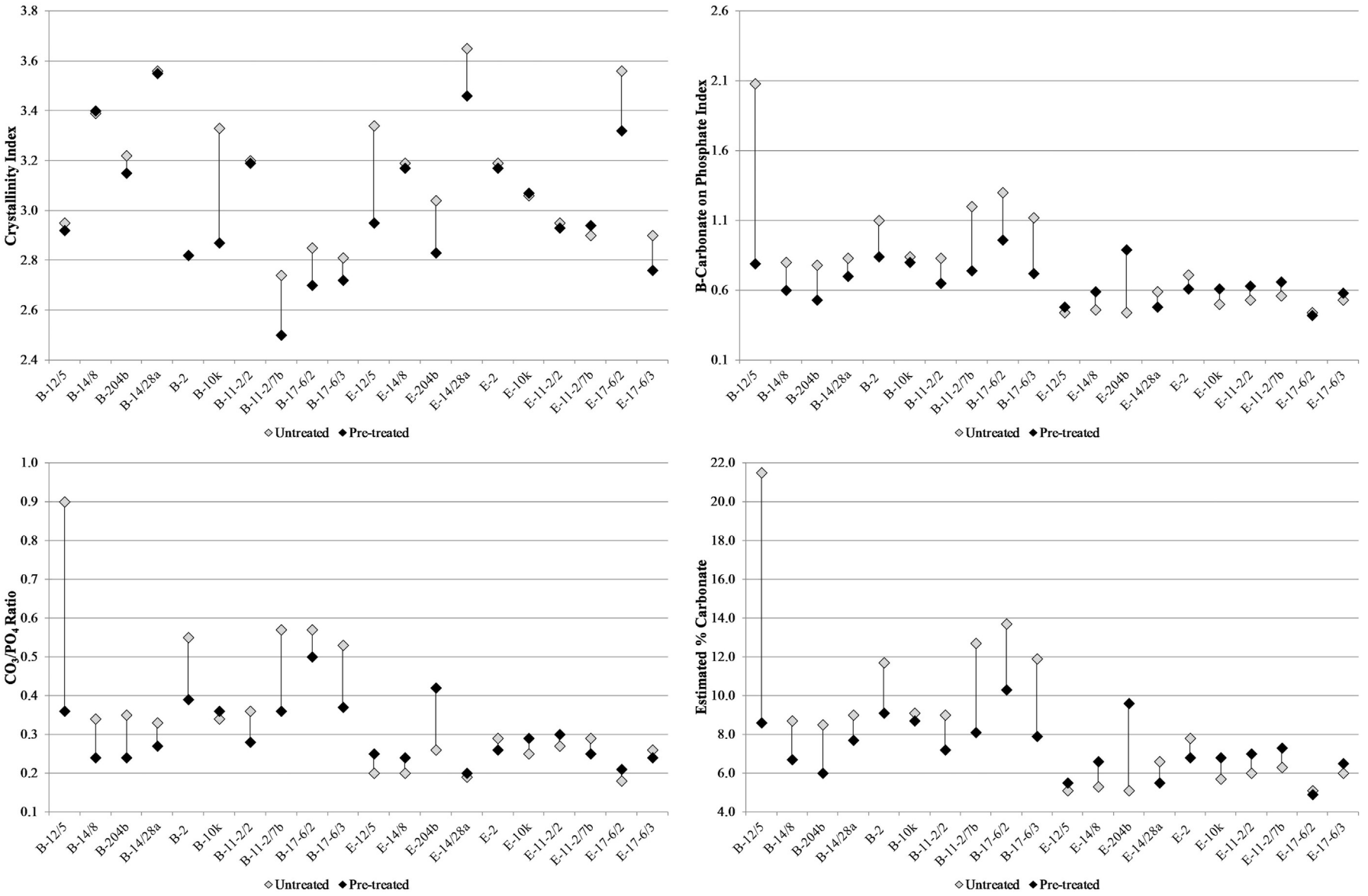

Fig. 3. Data from FTIR Parameters for CI, BPI, Estimated % Carbonate and CO_3/PO_4 Ratios (clockwise from top left).

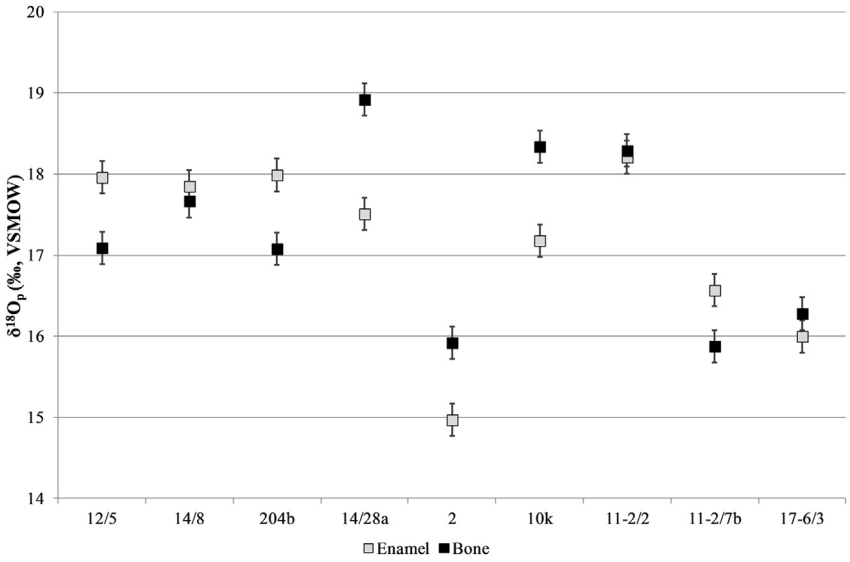

Fig. 4. Phosphate–oxygen isotopic results.

research. The average changes in carbon- and oxygen-isotope compositions for enamel and bone determined here are lower in magnitude and not consistent (i.e., ^{13}C- or ^{18}O-enriched or depleted relative to untreated samples) compared to the modern material analysed by Koch et al. (1997) and Garvie-Lok et al. (2004). Based on an examination of FTIR spectra and changes in FTIR parameters, the pre-treatment protocol used here is effective in removing diagenetic material. The shifts associated with pre-treatment, although small, are nonetheless large enough that consistency in pre-treatment within a research sample may be necessary if small changes in isotopic composition are to be considered interpretively important.

We have determined that there is a large, consistent offset between enamel and bone carbon-isotope compositions and, to a lesser extent, between enamel and bone oxygen-isotope compositions. The shift in oxygen-isotope compositions is similar to the offset reported by Warinner and Tuross (2009) for pigs in a controlled growth and feeding experiment (+1.7 ± 0.2‰ for pigs versus +1.4 ± 1.0‰ in this study). The shift in carbon-isotope compositions is considerably larger (+2.3 ± 0.4‰ for pigs versus. +4.3 ± 1.2‰ in this study), but similarly consistent in magnitude and in direction of the offset, i.e., enamel is always ^{13}C-enriched relative to bone. Differences between enamel and bone carbonate isotopic compositions have been observed in other studies (Howland et al., 2003; Passey et al., 2005). Although the precise magnitude and the cause of these differences could not be determined, differences between $\Delta^{13}C_{bioapatite\text{-}diet}$ for enamel and bone were attributed to lack of comparability between the two studies (Howland et al., 2003; Passey et al., 2005). In archaeological and ecological contexts, enamel and bone carbonate represent discrete windows of time during the organism's lifespan and are thus often expected to differ. In the present study, however, it is expected that formation and growth time of enamel and bone bioapatite will overlap, which limits the potential impact of seasonal dietary, digestive or ontogenetic effects on enamel and bone isotopic composition. Thus, having also eliminated significant, detectable post-mortem alteration as a potential cause of the inter-tissue offset, it is likely that the determinations made in this study are real.

The difference in the magnitude of fractionation of blood bicarbonate in enamel versus bone bioapatite may be caused by differences between the two tissues in bioapatite formation and maturation. As part of the mineralization process, hydrogen ions (H^+) are released into the surrounding aqueous fluid, which causes a significant increase in acidity. Bioapatite cannot, however, form in highly acidic solutions. For bone, dentine and cementum, it is generally assumed that hydrogen ions are either removed from the surrounding fluid via diffusion or that the surrounding tissues have a high buffering capacity and are able to neutralise the acid produced. In contrast, animal model research has determined that the amount of fluid surrounding enamel is comparatively small, possesses a different ionic composition than the fluid surrounding bone, and has a lower buffering capacity (Aoba and Moreno, 1987; Smith, 1998; Smith et al., 2005). To compensate for acidification, substantial amounts of bicarbonate ions are periodically released from the ameloblasts of the growing tooth in order to neutralise excess hydrogen ions that cannot be buffered by surrounding tissues or fluid (Simmer and Fincham, 1995; Smith et al., 2005). We suggest that this process may be sufficient to induce additional

Table 3
Phosphate–oxygen isotopic results.

Sample ID[a]	Ag_3PO_4 yield	CO_2 yield (μmol/mg)	$\delta^{18}O$ (‰, VSMOW)	Enamel–bone	|Enamel–bone|
B-12/5	0.71	5.33	17.1		
B-14/8	1.03	5.42	17.7		
B-204b	1.13	4.97	17.1		
B-14/28a	1.09	4.88	18.9		
B-2	0.92	4.98	15.9		
B-10k	1.15	4.86	18.3		
B-11-2/2	1.01	5.00	18.3		
B-11-2/7b	0.88	4.93	15.9		
B-17-6/3	1.08	4.95	16.3		
Average	1.0	5.0	17.3		
1σ	0.1	0.2	1.1		
E-12/5	1.27	5.21	18.0	0.9	0.9
E-14/8	1.12	5.35	17.9	0.2	0.2
E-204b	1.20	4.91	18.0	0.9	0.9
E-14/28a	0.80	5.60	17.5	−1.4	1.4
E-2	1.01	5.42	15.0	−0.9	0.9
E-10k	1.35	4.56	17.2	−1.2	1.2
E-11-2/2	0.86	4.80	18.2	−0.1	0.1
E-11-2/7b	1.17	5.03	16.6	0.7	0.7
E-17-6/3	1.04	5.04	16.0	−0.3	0.3
Average	1.1	5.1	17.1		0.7
1σ	0.2	0.3	1.1		0.5

[a] B: bone sample, E: enamel sample.

Table 4
Inter-tissue offsets for carbonate–oxygen and -carbon isotopic results and comparison of untreated vs. pre-treated bone and enamel.

Pre-treated samples				Pre-treated enamel − bone		Untreated samples		Pre-treated − Untreated	
Sample ID[a]	Yield (%)[b]	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)
B-12/5	77	−4.7	26.0			−5.0	25.8	0.3	0.1
B-14/8	92	−6.8	26.3			−7.1	25.1	0.3	1.2
B-204b	88	−7.3	25.8			−7.1	23.6	−0.2	2.2
B-14/28a	90	−6.9	26.4			−5.2	25.6	−1.7	0.8
B-2	83	−6.5	22.7			−6.7	23.4	0.2	−0.7
B-10k	93	−5.3	26.1			−5.4	25.2	0.1	0.9
B-11-2/2	90	−5.6	24.4			−5.5	24.1	−0.1	0.3
B-11-2/7b	77	−5.0	25.1			−5.5	25.3	0.5	−0.3
B-17-6/2	87	−5.1	25.1			−5.6	24.4	0.0	0.7
B-17-6/3	87	−5.6	25.0			−5.2	23.4	0.1	1.6
Average	86	−5.9	25.3			−5.8	24.6	−0.1	0.7
1σ	6	0.9	1.1			0.8	0.9	0.6	0.9
E-12/5	92	−1.4	28.0	+3.3	+2.0	−2.2	27.1	0.8	0.9
E-14/8	92	−0.7	26.7	+6.1	+0.4	−2.5	25.7	1.8	1.1
E-204b	100	−2.0	28.4	+5.3	+2.5	−2.5	27.3	0.5	1.2
E-14/28a	88	−4.3	26.7	+2.5	+0.4	−5.3	26.3	1.0	0.4
E-2	90	−4.1	26.0	+2.4	+3.2	−6.0	26.2	1.9	−0.1
E-10k	95	−0.1	26.4	+5.2	+0.3	−0.5	26.2	0.4	0.3
E-11-2/2	95	−0.7	25.9	+4.9	+1.5	−0.8	25.9	0.1	0.0
E-11-2/7b	96	−0.4	26.1	+4.7	+1.0	−1.1	24.8	0.7	1.3
E-17-6/2	93	−1.5	26.3	+4.1	+1.1	−2.1	25.4	0.6	0.9
E-17-6/3	97	−1.0	25.8	+4.1	+0.7	−1.1	25.6	0.1	0.2
Average	94	−1.6	26.6	4.3	1.4	−2.4	26.0	0.9	0.7
1σ	3	1.5	0.9	1.2	1.0	1.9	0.8	0.6	0.5

[a] B: bone sample, E: enamel sample.
[b] Calculated as (pre-treated sample weight/starting sample weight)*100.

fractionation between the isotopic compositions of enamel and blood bicarbonate, the outcome of which is enamel bioapatite that is ^{13}C-enriched relative to bone bioapatite.

6. Conclusion

Carbonate-carbon and -oxygen and phosphate-oxygen isotopic data are widely used in archaeological and palaeoenvironmental research to reconstruct palaeodiet, patterns of residential mobility, palaeoecology and past climate. In particular, the use of paired enamel and bone samples in archaeological contexts can be a valuable method of elucidating ancient migrations and residential histories. In this study, we have sought to determine if there is an inherent offset between enamel and bone carbon and oxygen isotopic compositions (either biological or induced by standard pre-treatment protocols) and, where possible, to quantify the magnitude of this offset. We have determined that the commonly-used FTIR spectroscopy indices (e.g., CI and CO_3/PO_4 ratios) remain useful tools for sample assessment. Further, they can be informatively supplemented with visual inspection of FTIR spectra, as well as other parameters (e.g., BPI), to allow a better understanding of diagenetic changes and efficacy of pre-treatment protocols. Pre-treatment for the removal of organic material and secondary carbonates does not induce large or consistent isotopic offsets, but does reduce sample size. This is a particular concern when higher resolution sampling, such as serial sampling of enamel, is required.

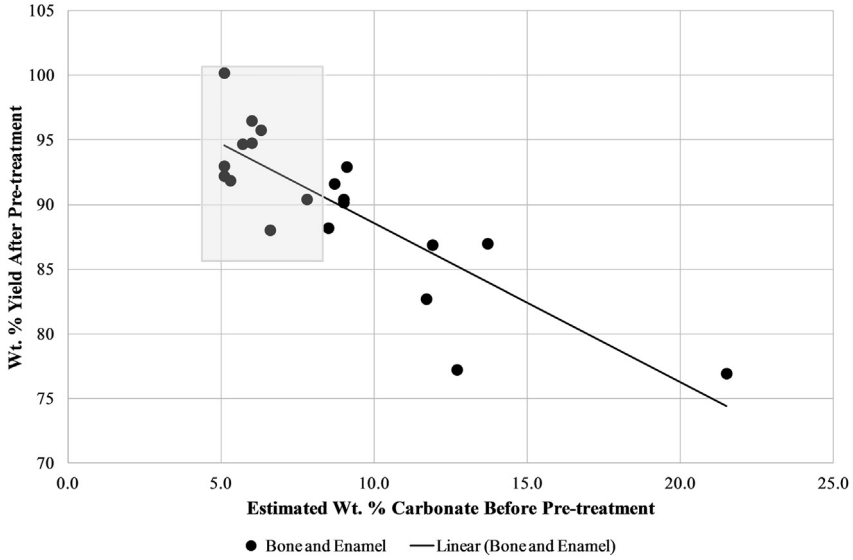

Fig. 5. Estimated Weight % Carbonate before Pre-treatment and Weight % Yield after Pre-treatment (grey box denotes enamel samples). Linear relationship is statistically significant (Pearson's $R = -0.837$, $p < 0.01$).

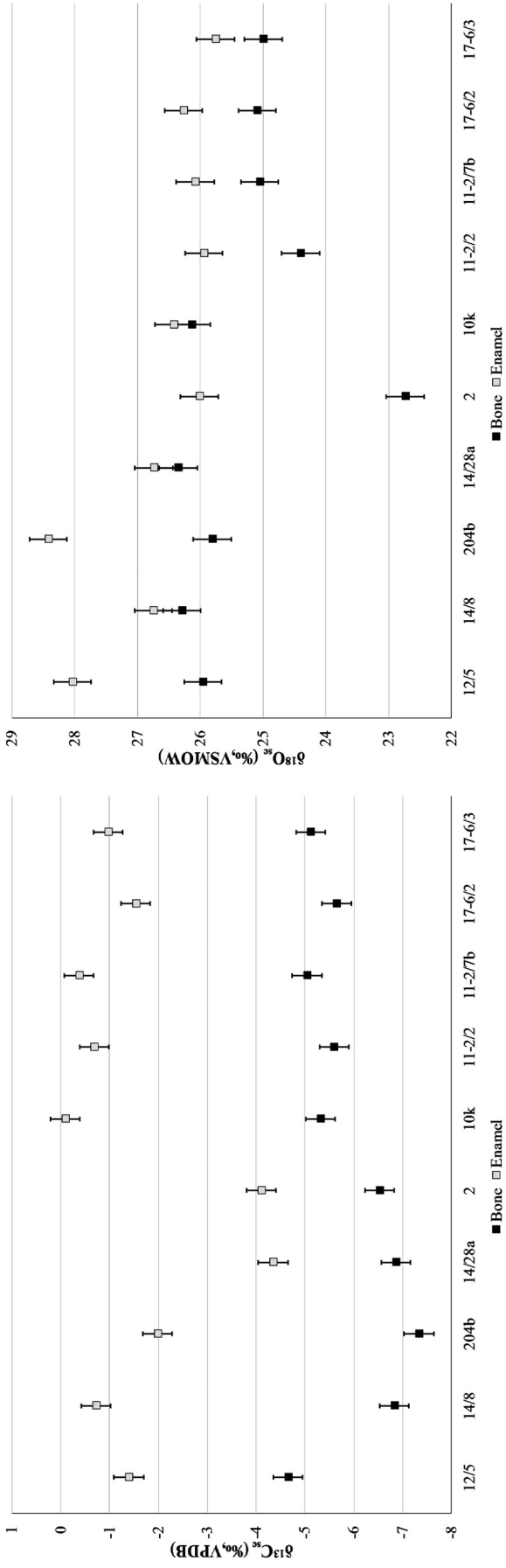

Fig. 6. Carbonate–carbon and –oxygen isotopic data.

The isotopic offsets for both carbon and oxygen are sometimes large enough that consistency in treatment may be a significant consideration, and sample assessment (e.g., by FTIR or some other means) of the need for full, partial (i.e., NaOCl treatment to remove organic material only), or no pre-treatment may be important.

In terms of phosphate-oxygen isotopic composition, bone and enamel bioapatite appear to be isotopically equivalent tissues. We have determined that there is a small offset between the two tissues (±0.7 ± 0.5‰), but neither enamel nor bone is consistently ^{18}O-enriched relative to one another. Phosphate-oxygen isotopic data thus seem to be well-suited to elucidating residential history and migration within an organism's lifespan through comparison of early-forming enamel and bone samples. Carbonate carbon- and oxygen-isotope compositions of bone and enamel bioapatite are, however, dissimilar. Enamel-bone differences of +4.3 ± 1.2‰ for carbon and +1.4 ± 1.0‰ for oxygen were determined for the samples included in this study. Enamel had a consistently higher isotopic composition than bone for all samples from both Marco Gonzales and San Pedro, suggesting a biological fractionation rather than diagenetic alteration or an offset induced by the methodology (e.g., pre-treatment and analysis). The difference between enamel and bone may be due to inherent differences in bioapatite crystallinity between the two tissues or to differences in the mineralization process, but further research is needed to determine the precise mechanism of ^{13}C- and ^{18}O-enrichment of enamel carbonate in humans. We suggest that enamel and bone carbonate isotopic data cannot be uncritically pooled or compared directly; moreover, given the variability in the magnitude of the offset, a correction factor cannot be determined at this time. Considered separately, however, bone and enamel (or multiple teeth from the same organism) remain an informative source of carbonate–carbon and –oxygen isotopic data.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jas.2014.07.001.

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